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13. ABSTRACT (Maximum 200 words) The motivation for this collaborative work with T. Sugama and co-workers at Brookhaven National Laboratory is to develop a low temperature ceramic coating process suitable for aluminum and magnesium. Their method uses sol-precursor solutions with polygermanosiloxane (PGS) or polytitanosiloxane (PTS) additive. Crosslinked networks are formed by pyrolytic reactions near 350°C. The surface microstructure of these films were investigated by Raman spectroscopy, AFM, SEM and EDAX. AFM scans of a 30% TSPI, 20% PTS ceramic film on Al 6061 showed prominent cracks, indicating imperfect match of Al and ceramic film thermal expansion coefficients. Single element scans of the surface reveal highest levels of Al occurring in the cracks, as would be expected because the ceramic film is thinnest at the cracks. However, the ceramic film may not be zero in the cracks, and may afford some level of corrosion protection, if the crack is not too wide. These studies indicate that obtaining crack free films is difficult. Optical spectroscopy showed evidence for Si-O-Ge linkages, and for interfacial oxane bonding with the substrate in the PGS films.				
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GROWTH AND MICROSTRUCTURE OF PROTECTIVE CERAMIC
FILMS ON ALUMINUM

FINAL TECHNICAL REPORT

BY
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U.S. ARMY RESEARCH OFFICE

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STATEMENT OF THE PROBLEM

The motivation for this work is to develop a low temperature ceramic coating process suitable for aluminum and magnesium. Ceramic coatings offer many advantages, but are not widely used on softer metals. A useful ceramic coating for Al or Mg should have a temperature expansion coefficient similar to that of the substrate metal, and the coating process should not require high temperatures. Many ceramic coatings must be applied or processed above 1000°C. Ceramic films possess the potential for both mechanical and corrosion protection for soft metals. To be useful the film must remain mechanically compact and adhere well to the metal substrate.

Sugama et al.^{1,2} have developed ceramic coatings for aluminum for corrosion protection with room temperature application and low temperature processing. The method uses sol-precursor solutions with polygermanosiloxane (PGS) or polytitanosiloxane (PTS) additive. Crosslinked networks are formed by pyrolytic reactions near 350°C.

The goals of the current effort are to investigate the surface microstructure of these films, and to relate the microstructure to composition and other film growth parameters. The techniques employed include Raman spectroscopy, AFM, SEM and EDAX.

SUMMARY OF THE MOST IMPORTANT RESULTS

The sequence for preparing a 30% N-3-[triethoxysilyl]propyl-4,5,-dihydroimidazole (TSPI) with 20% polygermanosiloxane (PGS) coating on an aluminum substrate is given below. This coating would be labeled as 30% TSPI, 20% PGS. Aluminum specimens used were nominally 1 cm² in area and 1 mm thick.

- washed with methanol, followed by acetone, and then tissue wiped
- etched by an alkaline solution consisting of 0.4wt% NaOH, 2.8 wt% tetrasodium pyrophosphate, 2.8 wt% sodium bicarbonate, and 94.0 wt% water, for 20 min. at 80°C
- washed at 35°C for 5 min.
- baked in a 50°C oven for 30 min.
- dipped in the following solution, with composition indicated, and slowly removed:

TSPI 30 wt%

Ge(OC ₂ H ₅) ₄	20 wt%
CH ₃ OH	30 wt%
Water	20 wt%
HCl	15 wt% of combine wt. of TSPI + Ge(OC ₂ H ₅) ₄

- baked at 150°C for 20 hrs.
- baked at 350°C for 30 min.

Similar coating can be prepared with titanium, in place of germanium, using titanium(IV) ethoxide, Ti(OC₂H₅)₄. The performance of PTS films appear to exceed those of PGS. Some specimens with larger areas will be used in future studies to assess possible imperfect wetting due to small surface area.

Sugama et al.^{1,2} found several factors were important for forming good films with strong adhesion to the substrate. They were as follows:

- high spreadability of the sol solution
- formation of PGS or PTS at the sintering temperature of 150°C
- enhancement of Si-O-Ge or Si-O-Ti linkages at the pyrolysis temperature of 350°C
- minimal amounts of organic by-products
- formation of an oxane bond from the PGS or PTS to the aluminum oxide.

Figure 1 illustrates the morphology of a 30% TSPI, 20% PTS ceramic film on Al 6061 obtained by AFM. Cracks are evident, indicating imperfect match of Al and ceramic film thermal expansion coefficients. Single element scans of the surface reveal highest levels of Al occurring in the cracks, as would be expected because the ceramic film is thinnest at the cracks. However, the ceramic film may not be zero in the cracks, and may afford some level of corrosion protection, if the crack is not too wide. These studies to date indicate that obtaining crack free films is difficult, requiring careful control of composition and processing.

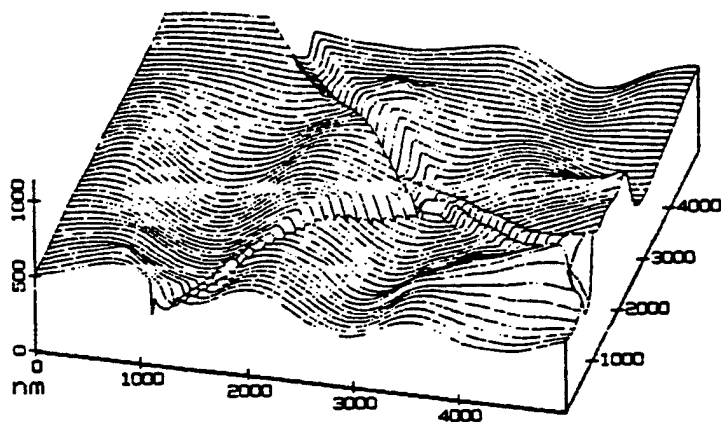


Figure 1. AFM scan of a 30% TSPI, 20% PTS ceramic film on Al 6061.

Optical spectroscopy showed evidence for Si-O-Ge linkages, and for interfacial oxane bonding with the substrate in the PGS films.

LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

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REPORT of INVENTIONS

None

LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL WITH ANY ADVANCED DEGREES EARNED BY THEM WHILE EMPLOYED ON THE PROJECT

Henry W. White, Principal Investigator

Jeffrey E. Chamberlain, Ph.D. August 1995

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